Nano Carbon Black and Activated Carbon from Agricultural Waste Filled Epoxy Composites

by

PARISHA FIROOZIAN

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LIST OF ABBREVIATIONS

H_3PO_4	Phosphoric Acid
BET	Brunauer–Emmett–Teller
S_L	Langmuir Isotherm
DGEBA	Diglycidyl Ether Of Bisphenol A
SEM	Scanning Electron Microscopy
KOH	Potassium Hydroxide
XRF	X-Ray Fluorescence Analysis
nm	Nano-Meter
µm	Micrometers
mm	Millimeter
EFB	Oil Palm Empty Fruit Bunches
CNS	Coconut Shells
BS	Bamboo Stem
AC	Activated Carbon
CB	Carbon Black
CF	Carbon Fiber
C	Carbon
H	Hydrogen
O	Oxygen
N	Nitrogen
S	Sulfur
FT-IR	Fourier Transform Infra-Red
Si	Silicon
K	Potassium
Mg	Magnesium
Ca	Calcium
EDX	Energy Dispersive X-Ray
TEM	Transmission Electron Microscopy
V	Voltage
DSC	Differential Scanning Calorimeter
TGA	Thermal Gravimetric Analyzer
CV-IV	Capacitance Voltage- Current Voltage
Tan ä	Damping Factor
E’	Storage Modulus
T_g	Glass Transition Temperature
OMMT	Organophilic Montmorillonite
PP	Polypropylene Blend
MPa	Mega Pascal
H_z	Hertz

LIST OF SYMBOLS

V_P	Total Pore Volume
S_{BET}	Brunauer–Emmett–Teller Surface Area
r	Average Pore Radius
W	Mass of Dry Adsorbent
P/P_O	Relative Pressure
m	Weight of Adsorbent
X_c	Degree of Crystallinity
A_c	Crystallized area
A_a	Amorphous area
δ	Delta

LIST OF PUBLICATION AND CONFERENCE

Komposit Epoksi Terisi Nano Karbon Hitam dan Karbon Diaktif Nano daripada Sisa Pertanian

Abstrak

Karbon hitam dan karbon diaktifkan yang berasal dari sisa pertanian seperti batang buluh (BS), tempurung kelapa (CNS) dan tandan kelapa sawit kosong (EFB) diperolehi dari pirolisis gentian asli tersebut pada suhu 700°C dan seterusnya diaktifkan dengan bahan pengaktif kimia iaitu KOH dan H_3PO_4. Kesemua jenis karbon hitam dan karbon diaktifkan yang disediakan akan dikaji dan digunakan sebagai pengisi dalam komposit epoksi. Sifat-sifat fizikal dan kimia karbon hitam dan karbon diaktifkan telah dikaji dengan menggunakan analisis termogravimetri (TGA), mikroskop pengimbas elektron (SEM), mikroskop transmisi elektron (TEM), Fourier berubah inframerah spektrofotometer (FT-IR), dan pembelauan sinar-X (XRD). Kesan pirolisis pada karbon hitam dan kesan dua bahan pengaktif kimia yang berbeza iaitu H_3PO_4 dan KOH ke atas karbon diaktifkan juga turut dikaji. Diperhatikan bahawa, pengaktifan KOH terbukti lebih berkesan daripada H_3PO_4 dan pengaktifan fizikal terhadap sisa pertanian mengakibatkan peratusan mesopores yang lebih tinggi serta luas permukaan yang lebih tinggi.

Komposit epoksi nano baru yang mempunyai sifat kekonduksian elektrik yang baik serta sifat mekanikal dan termal yang telah diperbaharui telah disintesiskan. Komposit epoksi yang terisi korbon hitam dan karbon diaktifkan telah dihasilkan dan pencirian bagi sifat-sifat mekanikal, morfologi, termal dan mekanikal dinamik juga telah dilakukan. Komposit-komposit epoksi yang terisi CNS-CB dan AC-CNS telah menunjukan sifat lenturan yang kebih baik berbanding komposit-komposit epoksi terisi karbon hitam dan karbon diaktifkan EFB-CB dan AC-BS

masing-masing. Komposit epoksi terisi CNS-CB dan AC-CNS mempamerkan sifat-sifat lenturan yang lebih baik berbanding dengan komposit epoksi terisi CB-EFB dan AC-BS dalam karbon hitam dan karbon diaktifkan masing-masing. Selain itu, EFB-CB dan AC-EFB menunjukkan sifat-sifat tegangan yang lebih baik daripada epoksi tulen, yang disebabkan oleh perlekatan yang lebih baik antara zarah dan matriks. Antara kemasukkan isipadu pengisi 1%, 5% dan 10%, 5% AC-CNS K menunjukkan kekuatan lenturan dan modulus yang lebih tinggi diikuti oleh AC-BS K dan AC-EFB K. SEM menunjukkan bahawa permukaan retakan komposit menandakan rintangan yang tinggi untuk pecah. Keputusan TEM mengesahkan penyebaran seragam pada kemasukkan pengisi 5% sebagai tambahan kepada saiz nano zarah karbon yang diaktifkan dan karbon hitam.

Keputusan TGA menunjukkan peningkatan dalam kestabilan haba karbon karbon hitam dan diaktifkan terisi komposit berbanding resin epoxy tulen. Peningkatan utama dalam kestabilan haba diperhatikan untuk 5% AC-EFB K iaitu lima kali lebih daripada epoksi tulen. Pemerhatian ini adalah disebabkan oleh peningkatan tahap crystallinity AC-EFB K terisi epoksi komposit, yang ditentukan oleh keputusan XRD.

Keputusan DMA telah menunjukkan peningkatan yang ketara modulus penyimpanan terutamanya dalam kes komposit epoksi yang terisi AC-CNS K berbanding komposit lain, diikuti oleh AC-BS K.

Nano Carbon Black and Activated Carbon from Agricultural Waste Filled Epoxy Composites

Abstract

Carbon blacks and activated carbons derived from agricultural wastes such as bamboo stem (BS), coconut shells (CNS) and oil palm empty fiber bunch (EFB), were obtained by pyrolysis of these natural fibers at 700 ^{0}C and subsequently activated with KOH and H_3PO_4. The various carbon blacks and activated carbons prepared were characterized and used as filler in epoxy composites. The physical and chemical properties of the carbon blacks and activated carbons were studied using thermogravimetric analyzer (TGA), scanning electron microscope (SEM), transmission electron microscopy (TEM), fourier transform infrared (FT-IR) and X-ray diffraction (XRD) of activated carbons and carbon black were also carried out. The effect of pyrolysis on carbon black and two different chemical activations by H_3PO_4 and KOH on activated carbons were also studied. It was observed that KOH activation proved more effective than H_3PO_4 and physical activation on agricultural wastes resulted in higher percentage of mesopores and higher surface area.

A novel epoxy nano-composite with good electrical conductivity and having improved mechanical and thermal properties was synthesized. The carbon black and activated carbon filled epoxy composites were prepared and characterized for mechanical, morphological, thermal and dynamic mechanical properties. The CNS-CB and AC-CNS filled epoxy composites exhibited better flexural properties compared with EFB-CB and AC-BS in carbon black and activated carbon filled epoxy composite, respectively. Also, EFB-CB and AC-EFB showed better tensile properties than the neat epoxy, which was attributed to better adhesion between the

particle and matrix. Among 1%, 5% and 10% by volume filler loading, 5% AC-CNS K showed higher flexural strength and modulus followed by AC-BS K and AC-EFB K. The SEM showed that the fractured surface of the composite indicates its high resistance to fracture. TEM results confirmed homogeneous dispersion at 5% filler loading in addition to nano-particle size of activated carbon and carbon black.

TGA results showed enhancement in thermal stability of the carbon black and activated carbon filled composites compared to the neat epoxy resin. The major improvement in thermal stability was observed for 5% AC-EFB K which is five times more than neat epoxy. This observation was attributed to the improved in the degree of crystallinity of AC-EFB K filled epoxy composite, determined by XRD results.

DMA results have shown significant improvement of storage modulus particularly in case of AC-CNS K filled epoxy composite as compared to other composites, followed by AC-BS K.

CHAPTER ONE

INTRODUCTION

1.0 Introduction

Polymeric materials have been filled with synthetic or natural inorganic compounds in order to improve their properties, or to reduce the cost of polymeric materials. The introduction of well-dispersed inorganic particles into a polymer–matrix has been confirmed to be extremely effective to improve the performance of the polymer composites (Allawar et al., 2008). Conventional fillers are materials in the form of particles (e.g. calcium carbonate), fibers (e.g. glass fibers) or plate-shaped particles (e.g. mica) (Pavlidou and Papaspyrides, 2008). In general, the composite materials contain two distinct phases: the base matrix and the dispersed (reinforcing) phase and having bulk properties significantly different from those of any of the constituents. Polymeric nanocomposites are produced by combination matrix and dispersed inorganic particles at least one dimension at the nano-scale (Giannelis et al., 1999). High performance polymer nanocomposites are emerging as a new class of materials for its demanding applications as insulating material, for which at least one dimension of the dispersed particles is in the nanometer range (<100 nm). In any case, nano-particles are added to the matrix or matrix precursors as 1–100nm powders, containing associated nano-particles composite.

Addition of nano-particles has become a common practice because at low nano-filler content, it improves mechanical and thermal properties of the resulting nanocomposites and also reduce processing cost (Pinnavaia and Bell, 2000; Komarneni, 1992; Enikolopyan, 1990; Jayatilaka, 1979). The improvement of nanocomposites strongly depends on the particle content, shape, size, surface area,

and degree of dispersion (Kornmann, 2001; Pinnavaia and Bell, 2000; Lan and Pinnavaia, 1994; Komarneni, 1992).

Polymeric composites with nano-sized filler had been used in high voltage electrical insulation system, and many result reports about the influence of nano-filler on the dielectric properties of the nanocomposites (Alexandre and Dubois, 2000; He et al., 2009). Epoxy resin is an indispensable material for insulation systems in power equipments like dry type transformers and rotating machines. The epoxy resin is used not only as insulating material but also as structural material because the material is cost-effective (Sarathi et al., 2007).

1.1 General Introduction

In fact, nanocomposites have been established with many thermoplastic and thermosetting polymers of different polarities including polystyrene, polycaprolactone, polypropylene, poly(ethylene oxide), epoxy resin, polysiloxane and polyurethane (Pavlidou and Papaspyrides, 2008). Several researchers reported on preparation and characterization of nano-filler based epoxy composites (Mirmohseni and Zavareh, 2010; Bakar et al., 2010; Palencia et al., 2011).

In-situ polymerization has also been explored to create thermoset based nanocomposites. This method has been extensively used for the production of both intercalated and exfoliated epoxy-based nanocomposties. Researchers have analyzed the effects of different curing agents and conditions in the formation of epoxy nanocomposites based on the diglycidyl ether of bisphenol A (DGEBA) and namontmorillonite modified by bis(2-hydroxyethyl) methyl tallowalkyl ammonium chloride (Messersmith and Giannelis, 1994).

Activated carbon is one of the most important adsorbents from an industrial view of point. The main application of this adsorbent is for separation and purification of gaseous and liquid phase mixtures (Ismadji and Bhatia, 2001). Agriculture based biomass are appropriate and inexpensive precursors for the production of activated carbon. Numerous successful attempts have been made to produce activated carbons (well-developed pore structures and high internal surface area) from various ranges of agricultural wastes such as wood, saw dust, bagasse, coconut shells, rice husk, rubber wood saw dust, oil palm shell and coir pith (Ioannidou and Zabaniotou, 2007).

The abundant supply of waste-product from the agricultural and desiccated industries makes production of activated carbon from these materials more financially viable, since using grain or coal as raw materials for activated carbon will require manufacturers extra investment for procurement. Activated carbon can be produced either through physical or chemical activation. In physical activation, the material is carbonized under inert atmosphere and then activated at high temperature using either steam or carbon dioxide as the activating reagent while in chemical activation, the precursor is treated with chemicals to help with the initial dehydration, but in most of the cases, chemical activation is preferred over physical activation as the latter generally results to lower yields due to the mass loss associated with oxidation (Toles et al., 2000).

In addition, chemical activation, which is commonly used for biomass precursor mainly because it achieves higher yield and larger surface areas, also requires lower operating and energy costs as lower temperatures are used. Chemical activation consists of carbonization at a relatively low temperature (400–700 °C) in the presence of dehydrating agents. These chemical reagents may promote the

formation of a rigid matrix, less prone to volatile loss and volume contraction upon heating to high temperatures. Among the numerous dehydrating agents for chemical activation, phosphoric acid is the most widely used chemical agent and preferred over the use of metal salts due to problems of environmental contaminations (El-Hendawy et al., 2008).

In addition activated carbons, obtained by chemical activation possess large surface area and well-developed microporosity, which can be controlled and maintained in narrow ranges (Budinova et al., 2006).The conversion of empty fruit bunch (EFB) to activated carbon will serve a double purpose. First, agricultural waste by-products is converted to useful, value-added adsorbents and second, it represents a potential source of adsorbents which will contribute to solving part of the wastewater treatment problems. However, there are limited studies reported on the utilization of EFB, especially on conversion of EFB into activated carbon (Rahman et al., 2007; Umikalsom et al.,2008).

Bamboo is an inexpensive and fast-grown resource with favourable physical and mechanical properties comparable to some common wood species. Bamboo has great potential as an alternative to wood for production of activated carbon for many adsorptive applications (Li et al., 2004). Coconut shells have little or no economic value and their disposal is not only costly but may also cause environmental problems. Coconut shell is suitable for preparing microporous-activated carbon due to its excellent natural structure and low ash content (Abdel-Aal et al., 2008a; Lua and Yang, 2004).

1.2 Problem Statement

The aim of this study is to compare and optimize the structural and material properties of the epoxy nanocomposites filled with carbon black and activated carbon from different sources. The lack of sufficient scientific information about the utilization of the raw materials (bamboo stem, coconut shell, EFB) for carbon production with enormous production of such agricultural waste materials were the driving force for the choice of this work.

There are numerals of reports on the utilization of activated carbon as adsorbents. Although, not much effort has been done on the utilization of activated carbon as nano-filler in polymer matrix and also researchers did not paid more attention on thermal studies of nano-filler reinforced polymeric materials. Utilization of agricultural waste such as oil palm, coconut, and bamboo to produce the activated carbon, which has low cost compare to the silica, alumina etc.

It is well known that activated carbons can be prepared using a variety of raw materials. The most commonly used precursors are coal, wood, coconut shells and agricultural byproducts. It has been reported that activated carbons prepared from agricultural byproducts more preferred than those other activated carbons used in the industry in terms of their properties, being cheap and renewable.

1.3 Scope of the Present Work

A combination of epoxy matrix with various types of nano-filler reinforcement materials lead to the development of epoxy nanocomposites which can be used in wide range of potential applications. Activated carbon/carbon black filled

polymer composites are lightweight materials, readily availability in different structural forms and are known to enhance the thermal, mechanical and electrical properties and the ease of fabrication of these composite through compression molding. Conventional conductive fillers such as carbon black (CB) and activated carbon (AC) are petroleum based and have been introduced into polymeric materials to modify their properties. Incorporation of these high thermally stable fillers into polymer matrix has been shown to be effective in the development of composites materials with improved thermal and mechanical properties. This research focus on development of high performance composites materials from biomass (agricultural wastes) materials with aimed to reduce the overall cost of the material preparation by using of inexpensive inorganic fillers.

1.4 Objectives

This research project is planned and carried out to address the following objectives:

a. To characterize various lignocellulosic materials (EFB, BS, CNS) as filler in high thermal stability epoxy composites.

b. To determine the physical, morphological and thermal properties of activated carbon and carbon black materials.

c. To study the morphological, mechanical properties, electrical and thermal stabilities of nano-carbon black filled epoxy composite materials.

d. To study the morphological, mechanical properties, electrical and thermal stabilities of nano-activated carbon filled epoxy composite.

1.5 Organization of Thesis

The thesis has been divided into eight chapters. The brief description and contents of the thesis (chapter-wise) are given below.

Chapter 1: This chapter gives an introduction of the present work. It also throws light on the background and justification of the work undertaken along with the objective of the present study.

Chapter 2: This chapter deals with the literature review of the present study. Review of activated carbon, carbon black and nano-filler polymer composite are given.

Chapter 3: In this chapter, consist of studied the physical and chemical properties of the raw material used for present research. Oil palm empty fruit bunches, bamboo stem, and coconut shell are the agricultural waste which are used for fabrication of carbon black/activated carbon based nanocomposites. Thermal and microscopy studies of agricultural biomass (coconut shells, bamboo stem and empty fruit bunch (EFB) are also included within this chapter.

Chapter 4: This chapter reported the preparation, characterization, thermal and microscopic studies of carbon black and activated carbon from agricultural biomass (coconut shells, bamboo stem and empty fruit bunch (EFB) using two different chemical activation processes (a) at 700 ^{o}C by phosphoric acid (H_3PO_4), (b) at 800 ^{o}C by Potassium Hydroxide (KOH) and also physical activation at 700 ^{o}C.

Chapter 5: This chapter reported the effect of the activated carbon under physical activation (Carbon Black) filled in epoxy composite by utilization of

thermal, mechanical, morphological and spectroscopic properties of 1% carbon black composites.

Chapter 6: This chapter deals about preparation of nano-activated carbon based epoxy composites and characterization viz., mechanical, dynamical and morphological properties of nano-activated carbon filled epoxy composite are determined while two different kind of activated carbon (AC by using H_3PO_4 and AC by using KOH) are compared. Comparison of thermal, spectroscopic, diffraction analysis properties of two different nano-activated carbon filled epoxy composite are given in this chapter.

Chapter 7: General conclusion and future study are given in this chapter. Overall conclusion of nano-activated carbon and carbon black epoxy composite was summarized in this chapter.

CHAPTER TWO

LITERATURE REVIEW

2.0 Literature

2.1 Biomass Material

Biomass, in the energy production industry, refers to living and recently living biological material, which can be used as fuel or for industrial production. Biomass conversion systems are arrangements, which can be large and produced electricity (bio-power) and heat; or small a wood stove or small wood-fired furnace using biomasses. Biomass conversion can also produce bio-fuels, which include ethanol, methanol, bio-oil, and bio-diesel. Biomass energy or bio-energy is the largest source of domestic renewable energy. Many Malaysian industries such as sugar, palm oil, rice, and wood have been utilizing their biomass as a fuel to cover some or all of their energy requirements (Ludovic and Sanjeeb, 2004). Oil palm biomass has been identified as one of the biggest resource that can be easily developed. Whereby, oil palm biomass contributes about RM 6379 million of energy annually. Despite its wide use already, there is still much to be done to optimize the utilization of biomass for cogeneration in Malaysia. Hence currently researches are churning out a wider variety of by-products as a result of continuous R&D efforts; making the downstream manufacturing into an industry itself. Whereby abundant waste biomasses are turned into renewable energy or value added products. This allows Malaysia to remain heads and shoulders above its other competitors. Figure 2.1 shows the scope of biomass initiatives (Sumathi et al., 2008).

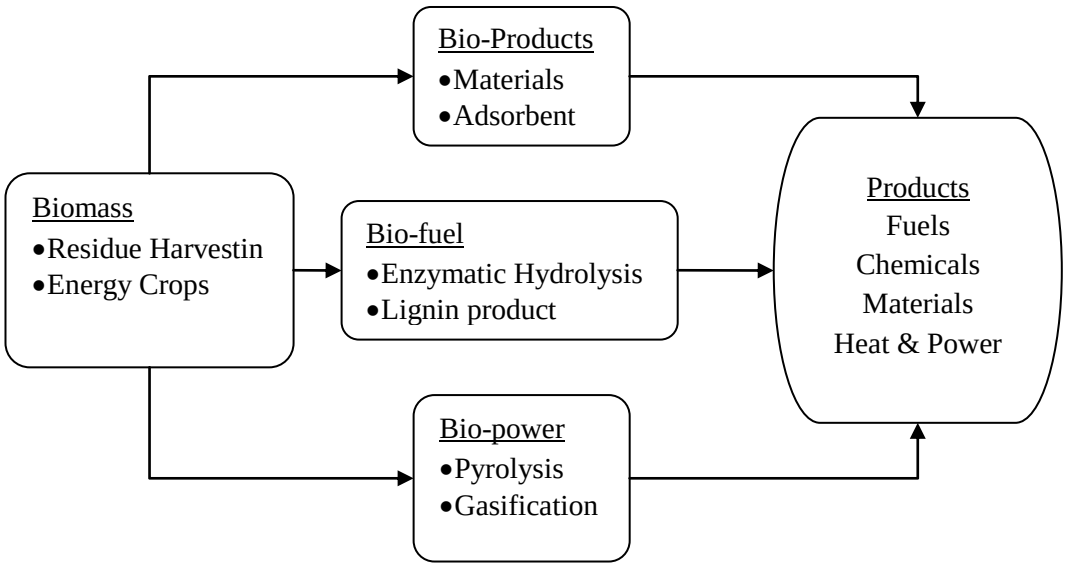


Figure 2.1: Biomass initiatives as renewable energy (Sumathi et al., 2008).

Oil palm biomass can be used to make the same products that are created by fossil fuels, sometimes using less energy to do so. Synthetic biofuels are synthetic hydrocarbons or mixtures of synthetic hydrocarbons from biomass, e.g. SynGas (SNG) produced from gasification of forestry biomass or SynDiesel (Rahman et al., 2006).

Bio-power is the use of biomass to generate electricity. Types of bio-power systems include direct-fired, gasification, anaerobic digestion, pyrolysis, and small, modular systems (Mohamad Husin et al., 2005).

Bio-related materials gain increasing importance also in the research and technology of polymer blends. Polymers from renewable resources, e.g. starch and cellulose, are used as components of blends or composites and attempts are made to produce biologically degradable polymers by the combination of such materials and polyesters produced by synthetic or natural processes. Results are still reported on

thermoplastic starch/polyolefin blends in spite of the fact that such materials were already produced in industrial scale since 15 years ago. Moreover, the ban of such materials is considered in some countries because they fear that the fine polyolefin powder forming during the degradation of such materials blocks the soil and hinders the penetration of water, or covers lakes ruining living environment. Blends containing starch or cellulose and aliphatic polyesters either from synthetic or microbial sources seem to have more potential in the future. However, considerable research must be done to improve their properties and decrease price. All cellulose composites may also develop to materials of some practical importance in the future, although the technology needs further development (Pukánszky, 2005).

The industrial bioenergy sector is also substantial in many countries and it is growing as regional and national government policies increasingly encourage the use of domestically available and renewable energy sources that minimize fossil fuel consumption. This industrial growth is accompanied by increasing concerns over whether or not environmental and social values are adequately ensured when biomass is grown, harvested, and converted to energy in both developing and developed countries. These concerns have resulted in increasing interest in the development of criteria and indicators (Stupak et al., 2011).

2.1.1. Empty Fruit Bunch (EFB)

Concern about environmental protection has increased over the years from a global viewpoint. Today, rapidly changing technologies, industrial products and practices generate waste that if improperly managed, could threaten public health and the environment. Undoubtedly, the agricultural waste biomass is currently one of the

most challenging topics, which gained extensive stern consideration during the past decades. In the above perspective, oil palm is rated top, with an annual fruit crop production of 36.90 million tons, corresponding to 35.90% of the total edible oil in the world (Foo and Hameed, 2009).

Bioconversion of lignocellulosic waste materials to chemicals and fuels are receiving interest as they are low cost, renewable and widespread in nature. Malaysia is well known for its potential in renewable resources such as oil palm waste, sugar cane bagasse and rice straw. In the process of extraction of palm oil from oil palm fruit, a lignocellulosic material oil palm empty fruit bunch (OPEFB) is generated as a waste product. Approximately fifteen million tons of OPEFB biomass waste is generated annually throughout Malaysia by palm oil mills. In practice this biomass is burned in incinerators by palm oil mills which create environmental pollution problems in nearby localities. The OPEFB biomass contains cellulose, hemicellulose and lignin. It is estimated that OPEFB biomass is comprised of 24% xylan, a sugar polymer made of pentose sugar xylose. This xylose can be used as substrate for production of a wide variety of compounds by chemical and biochemical processes (Rahman et al., 2007).

2.1.2. Bamboo Stem (BS)

Bamboo is a lignocellulosic resources material, used as a raw material for building, fuel, and various other uses. Its potential in production of commodity chemicals, bio-fuels and biodegradable materials has drawn attention recently, in view of research and technology advancement in bioengineering and material science. Traditionally bamboo has been viewed as an agricultural waste material or

underutilized tree crop with a low value product for pulping and paper industry. Its utilization as fuel fire bakery and house hold cooking is well known for ages. Bamboo is also use as scaffolding, furniture units, plywood, and ornamentals (Bhat et al., 2011).

Production and comparison of high surface area bamboo derived active carbons has reported by Ip et al.,(2008). In this research, high surface area activated carbons have been produced from the natural biomaterial bamboo, using phosphoric acid as the activating agent. The effects of phosphoric acid impregnation ratio, activation temperature, heating rate on the carbon surface area, porosity and mass yield are presented. They reported that heating rate, impregnation ratio and activation temperature are all sensitive conditions for the surface area development. For carbon producing at 600 ^{o}C, decreasing the heating rate can increase the surface area. Increasing the impregnation ratio can increase the surface area initially and then decrease the surface area. For carbon production with a heating rate of 5 ^{o}C/min, increasing activation temperature can increase the surface area when the impregnation used is less than 4. The most outstanding carbon was prepared using an impregnation ratio of 2, an activation temperature of 600 ^{o}C, an activation time of 4 h and a heating rate of 1 ^{o}C per minute, which produced the highest surface area carbon of 2123 m^2/g. They worked on the adsorption properties of this activated carbon (Ip et al., 2008).

Previous studied by (Hameed and El-Khaiary, 2008), (Krzesinska and Zachariasz, 2007), (Kubisz and Ehrlich, 2007) also fabricate the activated carbon from bamboo using chemical agent for same application although there are not any report for composite application.

2.1.3. Coconut Shell (CNS)

The total land area in Malaysia amounts to 32.90 million ha. The total land area under natural forest is 20.1 million ha (61%) and agriculture area is 4.89 million ha which is 14.9% of land area in Malaysia. The major agricultural crops grown in Malaysia are rubber (39.67%), oil palm (34.56%), rice (12.68%), cocoa (6.75%) and coconut (6.34%) (Ong et al., 2011). In Malaysia, expansion of palm oil production is said to have occurred primarily on logged-over forest and on former rubber and coconut plantations, while in Indonesia natural rainforest and peat land have often been converted for palm oil production. A recent estimate indicates that of all oil palm expansion between 1990 and 2005 in both countries, at least 50% has come at the expense of natural rainforest (Wicke et al., 2011).

In year 2001, about 151,000 ha land area being used for coconut plantation in Malaysia. Generally, coconut shells have used as fuel for coconut processing, as a source of fiber for rope and mats. To make better use of this cheap and abundant agricultural waste, it is proposed to convert coconut husk into activated carbon. Tan et al.,(2008) have reported the production of activated carbon from coconut husk using physiochemical activation method, consisted of potassium hydroxide (KOH) treatment and carbon dioxide (CO_2) gasification is the mesocarp of coconut and a coconut is consists of 33–35% of husk. Similar study has reported the production of activated carbon from coconut shell at different temperature by using the physical activation and revealed that surface area 1926 m^2/g at 1000 ^oC under N_2 gas (Li et al., 2008b). Researchers (Rosas et al., 2009, Daud and Ali, 2004) have concluded that the carbonization temperatures had great effects on the yields and pore development of the chars prepared. With increasing carbonization temperatures, more volatiles were released and more microporous were formed, giving rise to a

decrease in yield, and increases in the S_{BET} surface area, total volume and microporous volume of the char. It is reported that activated carbon from coconut shell by simultaneous physical and chemical activation to prepare mesoporous high-surface area which is very interesting candidates for versatile applications, such as water treatment, gas storage, battery electrodes, and catalyst support (Hu et al., 2000). The mesoporous carbons made in their study have several advantages: low-cost starting material, simple procedure, very high surface area and pore volume, and narrow pore size distribution (Hu et al., 2003).

2.2. Matrix

Matrix can be easily defined as a material where the reinforcing system of a composite is embedded. The matrix serves as a binder which holds the reinforcing materials in its place. The matrix also provides resistance to crack propagation and damage tolerance owing to the plastic flow at crack tips (Schwartz, 1992). Both thermosets and thermoplastics (including bio-derived ones) are attractive as matrix materials in the production of composites. Plastic matrices can generally be classified into two major types which are thermoplastics and thermosets. The selection criteria of the matrices depend on the composite end application. For example, if chemical resistance together with elevated temperature resistance is needed for a composite material then thermoset matrices are preferred than thermoplastics. Whereas, if a composite material with high damage tolerance and recyclability is needed then thermoplastics are preferred (Krawczak, 2008).

2.2.1. Thermoset Based Matrix

Much of the early work used thermosetting resins as matrix material for composite production. Thermoset resins are usually liquids or low melting point solids in their initial form. This liquid resin is then converted to a hard rigid solid by chemical cross-linking through a curing process which involves the application of heat and the addition of curing agents or hardeners. Once cured, a tightly bound three dimensional network structure is formed in the resin and hence the resin cannot be melted, reshaped and reprocessed by heating (Olivares-Marín et al., 2007). Therefore, during composite manufacturing, the impregnation process followed by the shaping and solidification should be done before the resin begins to cure (Liu et al., 2007). Thermoset resins are brittle at room temperature and have low fracture toughness. On the other hand, owing to its three dimensional cross linked structure, thermoset resins have high thermal stability, chemical resistance, high dimensional stability and also high creep properties (Schwartz, 1992). Among the most common thermosetting resins used in composite manufacturing are unsaturated polyesters, epoxies, vinyl esters and phenolics. Typical properties of four thermoset resins are tabulated in Table 2.1.

Table 2.1: A comparative study of the properties of Epoxy, unsaturated Polyester, Vinyl ester, and Phenolic Resin (Dipa and Jogeswari, 2005).

Properties	Unsaturated Polyester Resin	Epoxy Resin	Vinyl Ester Resin	Phenolic Resin
Density(g/cc)	1.2-1.5	1.1-1.4	1.2-1.4	1.3
Tensile Strength (MPa)	40-90	35-100	69-83	10
Young's modulus (GPa)	2-4.5	3-6	3.1-3.8	0.375
Elongation at break (%)	2	1-6	4-7	2
Compressive Strength (MPa)	90-250	100-200	-	-
Cure Shrinkage (%)	4-8	1-2	-	-
Water absorption 24 hr at 20^0C	0.1-0.3	0.1-0.4	-	-
Fracture Energy (kPa)	-	-	2.5	-

To achieve reinforcing effects in composites it is necessary to have good adhesion between the filler and matrix. Composite manufacture can be achieved using low viscosity epoxy and phenolic resins that cure at room temperature. In addition epoxy resin does not produce volatile products during curing which is most desirable in production of void free composites. Therefore, although epoxy resins are relatively more expensive than unsaturated polyester, they have potential for the development of high added value composites.

In this paragraph the comparative study of the advantages and disadvantages of thermosetting resins is briefly discussed. Unsaturated polyester as the first matrix is easy to use with the lowest cost of resins available (€ 1-2/kg) but this matrix only provide moderate mechanical properties. In addition using unsaturated polyester has resulted in high styrene emissions in open molds. Therefore it needs high cure shrinkage and consequently the range of working times is limited. Vinyl ester is a

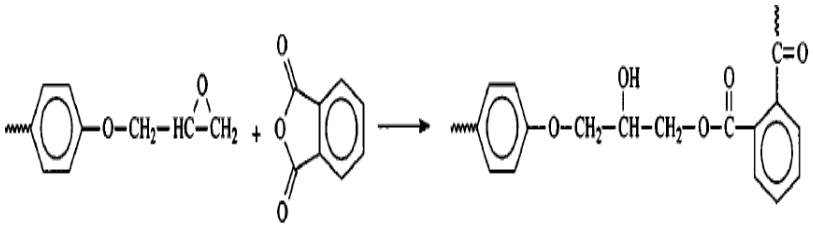
matrix which is chemical/environmental highly resistant and its mechanical properties are higher than unsaturated polyesters. As for disadvantages is that post cure generally required for high properties and high styrene content, high cure shrinkage and the price is higher than unsaturated polyesters (€ 2-4/kg). Epoxy has higher mechanical and thermal properties, high water resistance, and unlike polyesters low polymerization shrinkages during cure. Epoxy with excellent resistance to chemicals and solvents provide long working time, and excellent adhesion to fibers. Being more expensive than vinyl esters (€ 3-15/kg), critical mixing and corrosive handling should be considered as disadvantages of epoxy (Dipa and Jogeswari, 2005).

2.2.2. Epoxy Resin

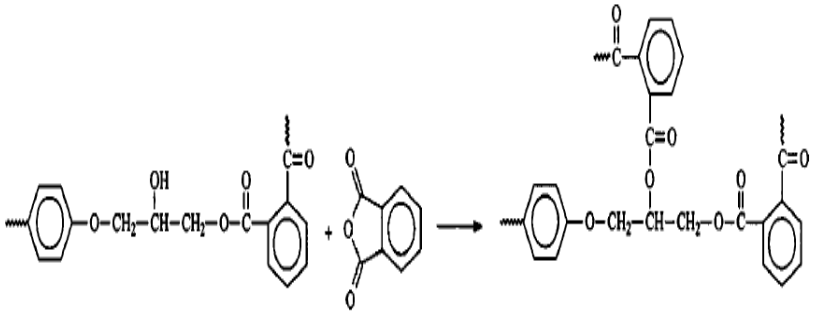
Epoxy resins are basically characterized by the presence of epoxide groups prior to cure, and they may also contain aliphatic, aromatic or heterocyclic structures in the backbone. Epoxy resins are relatively expensive; but, the long service time and good physical properties are very likely to help by providing a favorable cost–performance ratio in comparison to other thermosets. The main fields where fire-retardancy of epoxy resins is required are electronics (printed wiring boards and semiconductor encapsulation) and transportation (automotive, high speed trains, military and commercial aircraft) in composite structural and furnishing elements. Like other thermoset resins, epoxy resins can be rendered fire-retardant either by incorporating fire-retardant additives or by copolymerization with reactive fire retardants (Sergei V Levchik, 2004).

2.2.2.1. Structures and Cross-Linking of Epoxy Resins

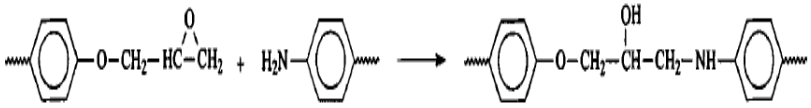
In order to understand the thermal decomposition and combustion of epoxy resins, here it will be briefly discussed the main structural elements and constituents of the cured epoxy network (Figure 2.2). The structure of the cured resin depends on the epoxy monomer and curing agent used. Usually, chemical linkages generated by reactions of glycidyl ethers are less stable than other chemical linkages in the epoxy network, and therefore there is justification to discuss here only those structures formed by the glycidyl ethers. Carboxylic acids easily react with epoxies; however, generally anhydrides are used for curing (Scheme 1). Anhydrides of dicarboxylic acids produce linear structures with diepoxides, and crosslinking often occurs because of esterification of the alcohol groups (Scheme 2). Aliphatic and aromatic diamines are the most widely used classes of curing agents. With the proper catalyst, aliphatic diamines cure epoxies at room temperature, whereas elevated temperatures are required for aromatic diamines (Scheme 3). Secondary amines, although more hindered than primary amines, can still react with epoxies and form crosslinks. Aliphatic alcohols are reactive with epoxies; however, they are not normally used as curing agents, In this article (Sergei V Levchik, 2004) were reported the thermal stability increases with increasing crosslink density.



Scheme 1.



Scheme 2.



Scheme 3.

Figure 2.2: Cross linking of epoxy resin with hardener(Sergei V Levchik, 2004).

The thermal stability of cured epoxy resins is greatly affected by the curing agent used. Thermal decomposition of any epoxy resin starts from the dehydration of the secondary alcohol in the aliphatic part of the resin, which leads to the formation of vinylene ethers. The next step of thermal decomposition is splitting of either the ether or amine bonds, weakened by the allylic groups. Evolution of highly combustible small aliphatic fragments follows. Some of the aromatic structures left can literally undergo charring. In the presence of flame-retardant additives, the thermal decomposition accelerates, although the amount of solid residue increases.

The combustion performance of epoxy resins is too much affected by the cross-linking density. Generally speaking, epoxy resins cured with anhydrides are more flammable than epoxy resins cured with amines. The oxygen index tends to be positively correlated to the char yield (Sergei V Levchik, 2004).

The most widely used curing agents for epoxy resins are primary and secondary amines. The overall reaction rate of an amine with an epoxide is influenced by the steric hindrance and the electron withdrawing or electron donating groups present in the amine (Patel et al., 1988). Anhydride, Dicyandiamide, polysulfide and polyamides are also used as curing agent in preparation of epoxy matrix.

2.3. Reinforcement (Organic and Inorganic Filler)

Particulates, henceforth called filler, can be classified into two categories: inorganic fillers and organic fillers. The fillers on different scale lengths and relates to the specific reinforcing properties of a base material is termed as reinforcing filler. The most commonly used inorganic fillers are low-cost minerals, such as talc and mica that are abundantly available in nature (Mallick, 2000). Most of the fillers used are inorganic and most are of mineral origin. The introduction of inorganic nano-particles as additives into polymer systems has resulted in polymer nano-composites (PNs) exhibiting multifunctional, high-performance polymer characteristics beyond what traditional filled polymeric materials possess (Joseph, 2006).

By comparing with inorganic fillers, the main advantages of lignocellulosics are as follows;

– Renewable nature

– Wide variety of fillers available throughout the world

– Nonfood agricultural based economy

– Low energy consumption

– Low cost

– Low density

– High specific strength and modulus

– High sound attenuation of lignocellulosic based composites

– Relatively reactive surface, which can be used for grafting specific groups.

The recycling by combustion of lignocellulosic filled composites is much easier in comparison with inorganic fillers systems. Therefore, the possibility of using lignocellulosic filler as reinforcing phase has received considerable interest. Fillers are inorganic or organic non-reactive compounds that are added to the polymer during the final stages of processing in order to reduce the flammability and improve mechanical, thermal or electrical properties of the finished product. The filler particles are under 10 μm in diameter, and often in the submicron range. The particles are blended into the liquid resin and must be uniformly dispersed in order to ensure consistent flame retardant properties throughout the polymer. Usually polymers require a high loading of filler to show an appreciable improvement to their flammability resistance, and the minimum volume content is usually about 20% and the average content is typically 50 to 60%. Fillers should only be used in polymers which are chemically compatible, otherwise the mechanical properties and

environmental durability of the material can be severely degraded. Fillers can have other deleterious effects on the properties, including an increase to the viscosity and a reduction to the gel time of the polymer melt which makes processing much more difficult. Many filler materials gradually break-down when exposed to moisture by hydrolysis, and this degrades their flame retardant action. Despite these problems, fillers are usually used because of their low cost, relatively easy addition into the polymer, and high fire resistance. It is important to note that fillers are rarely used alone, but instead they are used in combination with other flame retardants (such as organohalogen or organophosphorus compounds) to achieve a high level of flammability resistance. There are two classes of fillers - 'inert' and 'active' flame retardants – which are distinguished by their mode of action. Inert fillers reduce the flammability and smoke yield of polymer composites by several mechanisms. The dominant mechanism is reducing the fuel load by diluting the mass fraction of organic material in a composite by the addition of non-combustible filler. Flame retardation and smoke suppression by this mechanism can only be achieved when the polymer content is reduced by a large amount, and for this reason filler loadings of 50-60% are often required.

Another important mechanism is the absorption of heat by the filler to reduce the burning rate of the polymer matrix. To be an effective heat sink the filler must have a greater heat capacity than the polymer host. Certain fillers also reduce the flammability by forming an insulating surface layer when the polymer is decomposed and vapourised from between the filler particles. The layer reduces the rate of heat conduction to the underlying composite material, and therefore slows the decomposition rate of the polymer matrix. This surface layer can also obstruct the flow of combustible volatiles from the material into the flame, and thereby further

reduce the rate of decomposition. All fillers basically operate by reducing the mass content of polymer and most filler also act as a heat sink. Only a few types of fillers are capable of forming a surface layer that provides a high degree of thermal insulation and acts as an impervious gas barrier. The inert fillers most commonly used in polymers and polymer composites are silica, calcium carbonate and carbon black for their ability to reduce the flammability and smoke yield by the fuel dilution/heat sink mechanisms. In a few cases, simple hydrated clay silicates such as pumice, talc, gypsum and calcium sulphate dihydrate are used (Mouritz and Gibson, 2006).

The decomposition temperature of the filler is a critical factor in their efficacy as a flame retardant. The decomposition temperature must be higher than the processing temperature of the polymer matrix, otherwise the filler will decompose during manufacture of the composite material. Composites containing a high temperature thermoplastic resin, such as polyphenylene sulphide or polyether ether ketone, must be processed in the range 300-400 ^{o}C, and therefore require a filler material having a decomposition temperature above this range. However, the decomposition temperature of the filler must be below the pyrolysis temperature of the polymer matrix, which for many resins used in composites is between 300 and 450 ^{o}C (Mouritz and Gibson, 2006).

The fillers form chemical as well as physical crosslinks with the polymer chains, because of which the polymer segments in a certain zone around the filler experiences certain immobilization. This complex crosslink clusters prevent the rearrangement of the polymer chains during solvent ingression and reduces the free volume in the composite, thereby causing resistance to the path of penetrates. Figure

2.3 gives a schematic representation of the filler reinforced polymer matrix (Priya et al., 2008).

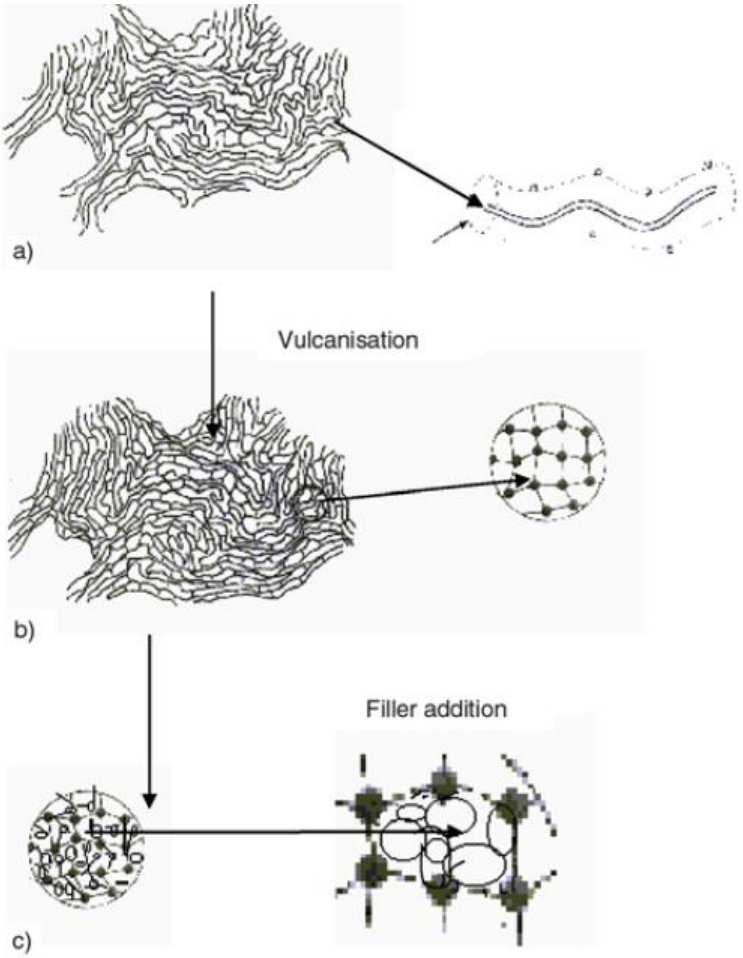


Figure 2.3: Pictorial representation of (a) unvulcanized polymer, (b) vulcanized polymer, (c) filled polymer (Priya et al., 2008).

2.3.1. Particulate Filled Polymers

Fillers and reinforcements were used in thermoset matrices and thermoplastic polymers. In particulate filled polymers two types of interactions may be distinguished. Particle–particle interactions lead to aggregation, while matrix–filler interactions determine micromechanical deformation processes as well as the macroscopic behavior and performance of the material (Pukánszky, 2005). In particulate filled polymers the dominating micromechanical deformation process is